

## EXPERIMENTAL INVESTIGATION OF EMISSIONS AND REDISTRIBUTION OF ELEMENTS IN CdTe PV MODULES DURING FIRES

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**ABSTRACT:** This study is based on glass-glass CdTe PV modules which are the only ones in the market. Pieces of commercial CdTe photovoltaic (PV) modules, sizes 3.8 cm by 30.5 cm, were heated to temperatures up to 1100°C to simulate exposure to residential and commercial building fires. The temperature rate and duration in these experiments were defined according to standard UL and ASTM test protocols. Three different types of analysis were performed: measurements of sample weight loss as a function of temperature; analyses of Cd in the fire emissions; and analysis of Cd distribution in the molten glass, using Synchrotron x-ray fluorescence microprobe. It was found that a small amount of cadmium compounds (0.4 to 0.6% of the Cd content) was carried to the edges by the flow of EVA decomposition products. The pathway for this loss was through the perimeter of the sample before the two sheets of glass fused together. In actual size PV modules, the ratio of perimeter to area is 13.5 times smaller; thus the actual Cd loss during fires would be insignificant (<0.04% of the Cd content).

Keywords: CdTe, Environmental Effect, Thin Film

### 1 INTRODUCTION

Fires in residential and commercial properties are not uncommon. If such fires involve the roof, photovoltaic arrays that are mounted there will be exposed to the flames. Subsequently, health hazards may arise from inhalation of toxic fumes and vapors if photovoltaic materials decompose or vaporize during a fire. Previous thermogravimetric studies of CdTe at the GSF Institute of Chemical Ecology in Munich, Germany, involved pure CdTe and a small number of tests on single glass PV modules [1,2]. The pure CdTe tests have shown a small weight increase between 570 °C and 800 °C, possibly due to oxidation. The oxidized product remained stable until about 1050 °C, above which the compound began to oxidize. Other experiments at non-oxidizing conditions (Ar atmosphere), showed a high loss of CdTe in the 900 to 1050 °C range. No experiments involving CdTe encapsulated between two sheets of glass are reported. The current study is based on glass-CdTe-glass PV modules, which are the only ones in the market. (Single-glass panels are not considered by any manufacturer at this time). Pieces of commercial CdTe photovoltaic (PV) modules, nominally 3.8 cm by 30.5 cm, were heated to temperatures up to about 1100 °C to simulate exposure to residential fires. The heating rate and duration in these experiments were defined according to standard UL and ASTM test protocols. The amounts of Cd and Te releases to the atmosphere were calculated by capturing these elements in nitric acid and hydrochloric acid-hydrogen peroxide solutions and the total loss was calculated by weight measurements. Also, the distribution of Cd in the burnt pieces were measured with x-ray synchrotron microprobe analysis.

### 2 THERMOGRAVIMETRIC TESTS

Typical flame temperatures in residential fires are in the 800-900 °C range for roof fires and in the 900-1000 °C in fires involving the whole house as measured in basement rooms [3]. In this study we extended this range to the limit of our heating apparatus, which was 1100 °C. The composition of the tested modules is shown in Table 1. These were standard commercial modules produced by First Solar L.L.C.

Table 1: Composition of Samples

Compound	Wt %
Total glass	96.1
EVA	2.5
Total Cd	0.059
Total Te	0.075
Total Cu	0.010

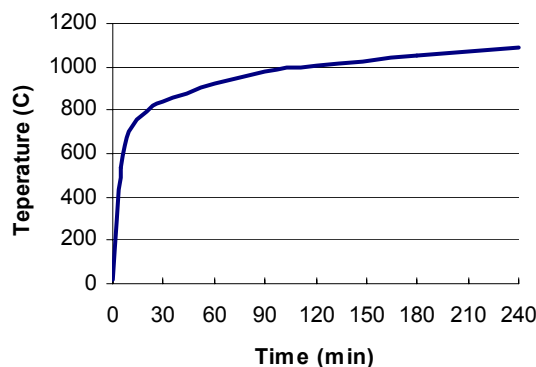


Figure 1. •Temperature and Heating Duration for Each Experiment (as per ASTM E119-98 Standard)

## 2.1 Protocol

There are several validated fire test methods used by the industry and the government in evaluating flammability and fire resistance of materials. Two test methods which are applicable to our task are the Underwriters Laboratories Inc., UL Standard 1256 for Fire Test of Roof Deck Constructions, and the American Society for Testing and Materials (ASTM) Standard E119-98 for Fire Tests of Building Construction and Materials. The latter is also adopted by the Uniform Building Code as UBC Standard No. 7-1. The UL 1256 Standard involves direct fire heating at 760 °C, for 30 minutes. The ASTM Standard involves gradual heating controlled to conform to the standard time-temperature curve shown in Figure 1. Our tests were done in a tube-furnace where we adjusted the heating rate to follow this standard temperature rate curve as closely as possible. The heating duration and maximum temperature for each experiment are shown in Figure 1.

Pieces of commercial CdTe photovoltaic (PV) modules, nominally 1.5" x 12", were used. The furnace was heated by electrical resistance and contained three-zones so uniformity of the central heated-zone was accomplished. The pieces of PV module were placed on alumina plates and were positioned inside a quartz tube in the central uniform temperature zone of the oven. The tube was fitted with an inlet and outlet for gas flow and was sealed from the outside atmosphere. Air was introduced into the furnace at a rate of 10 LPM, producing a linear velocity of 0.1 m/s above the sample. The airflow carried any released vapor/aerosols from the PV module to the outlet. The effluent flow was passed through a glass-wool filter and two bubbler-scrubbers in series containing a 0.01 M nitric acid solution in order to capture the Cd and Te releases from the PV module. The quartz tube and glass-wool were leached for 24 hours in nitric acid. Complete removal of the metals from the glasswool filters was realized by additional leaching using hydrochloric acid and hydrogen peroxide solutions for 48 hours in a tumbling machine.

## 2.2 Results

The acidic solutions from rinsing of the reactor walls, rinsing of the glasswool filters in the reactor exhaust, and the scrubber liquids, were analyzed for Cd and Te by Inductively Coupled Plasma- Optical Emission Spectroscopy (Varian Liberty 100).

The PV samples were measured before and after each experiment. Weight loss in the range of 1.9% to 2.2% of the total weight was recorded (Table 2).

The nitric acid solution from each scrubber and the rinse of the tube and the glass-wool filter were analyzed via ICP for Cd and Te. The concentrations in the second

scrubber were always zero, showing that the glass wool and the first scrubber captured the emissions. A small loss of Cd amounting to 0.4% to 0.6% of the total Cd in the sample was recorded (Table 2).

Measurements of the total mass of Cd and Te in the untreated sample were obtained by breaking the sample and leaching the metal content in a tumbling machine with a solution of sulfuric acid and hydrogen peroxide. Complete leaching of the metals was verified by leaching with hydrochloric/H<sub>2</sub>O<sub>2</sub> solutions. The uncertainty of the ICP analysis was determined by frequent calibration to be less or equal to 5%.

Table 2. Measured Loss of Mass

Test #	T (°C)	Weight Loss (% of sample)	Cd Loss (% of Cd in sample )
1	760	1.9	0.6
2	900	2.1	0.4
3	1000	1.9	0.5
4	1100	2.2	0.4

## 3. MICROBEAM X-RAY FLUORESCENCE ANALYSES

Slices were cut from the center and the sides of the burnt samples and were analyzed by microbeam x-ray fluorescence at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory.

### 3.1. Method

The incident beam was tuned to 26.8 keV with a Si (111) monochromator. This energy allowed excitation of Cd but not Te. Regions-of-interest were defined for Cd, Ca, Zr, and Sr K $\alpha$  x-rays. The spot size was focused to 30  $\mu$ m x 30  $\mu$ m using Rh coated Kirkpatrick-Baez mirrors. Energy dispersive SXRF data were collected using a Canberra SL30165 Si(Li) detector. Incident beam flux was monitored using an ion chamber and changes in fluorescent count rate with time were corrected by normalizing to the ion chamber current values.

Samples were 1 mm thick slices of the samples. They were mounted on Kapton tape and placed in a slide holder, with the sample directly exposed to the beam for analysis. Data were collected in two ways. Line scans were produced by rastering across a specific area of the sample, in steps that ranged between 20 and 50  $\mu$ m, depending on line length. Count times were varied from 5 to 10 seconds/ pixel. Data are presented as normalized Cd counts (Figures 2 to 5). This technique has detection limits on the order of 1 ppm.

### 3.2. Results

Figure 2 shows Cd counts in a slice cut from the control (unheated) sample. The Cd counts in the junction between the two sheets of glass reach a maximum of 50,000 while the Zr counts (indicative of the glass) in the

same region are close to zero. Figure 3 shows the Cd spectra in the center and the sides of a slice cut from the middle of the 760 °C PV sample. The Cd count distribution in the center was approximately the same as the distribution in the unheated sample, whereas the distribution near the sides shows diffusion of Cd in a wider area. Microscopic analysis showed that a gap was created near the edges of the slice; thus, a likely path for Cd loss is from the perimeter of the sample before the two pieces of glass melted together.

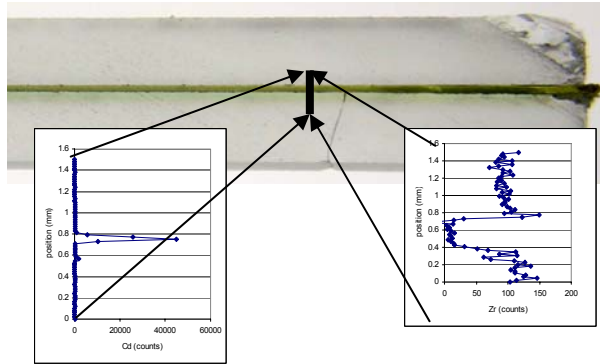


Figure 2. x-Ray Fluorescence Microprobe Analysis-Vertical Slice from Unheated (Control) Sample; Cd and Zr counts

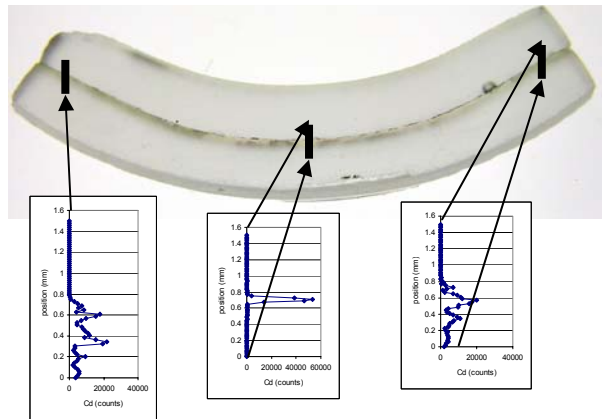


Figure 3. x-Ray Fluorescence Microprobe Analysis-Vertical Slice from Middle of Sample heated at 760 °C; Cd counts in the center and the sides of the slice.

Figures 4 show microprobe results, of a center section from the 1000 °C sample. It is shown that Cd moved to considerable depths into the molten glass and “froze” there after it cooled. At the highest temperature we tried (1100 °C) Cd diffused into greater depths around the junction (Figure 5). It appears that the higher the temperature the higher the convection/diffusion fluxes of Cd into the glass. As shown from the emissions analyses, the Cd loss was the same in all the experiments, so it appeared that the element was trapped to the same extent into the glass independently of the temperature, in

the temperature range of 760 °C -1100 °C).

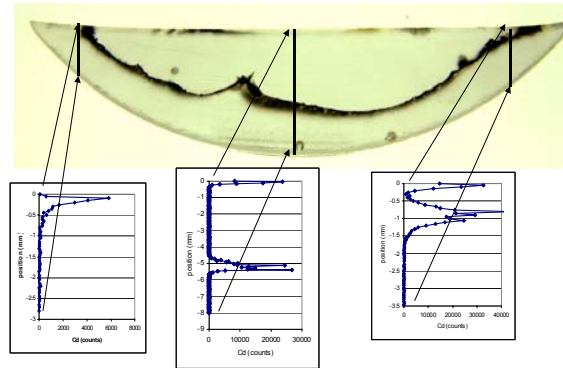


Figure 4. x-Ray Fluorescence Microprobe Analysis-Vertical Slice from Middle of Sample heated at 1000 °C; Cd counts in the center and the sides of the slice

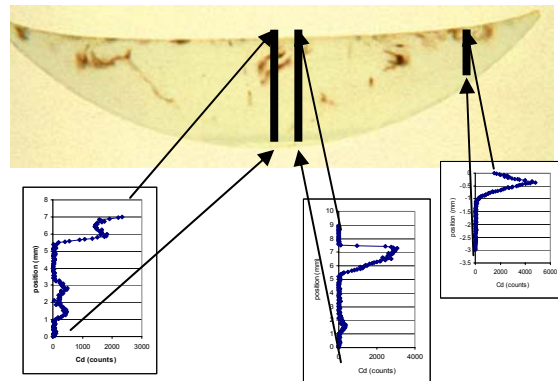


Figure 5. x-Ray Fluorescence Microprobe Analysis-Vertical Slice from Middle of Sample heated at 1100 °C; Cd counts in the center and the sides of the slice

#### 4 CONCLUSION

Most of the EVA was released during the experiments. Emissions analysis and x-ray microprobe synchrotron analysis showed that cadmium was effectively captured into the molten glass. A very small amount of cadmium compounds ( $0.5 \pm 0.1\%$  of the Cd content) was carried to the edges by the flow of EVA vapors and/or aerosol. The pathway for this loss was through the perimeter of the sample before the two sheets of glass fused together. In actual size PV modules, the ratio of perimeter to area is 13.5 times smaller; thus the actual Cd loss during fires would be  $\sim 0.04\%$  of the Cd content. Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the U.S. (e.g.,  $10^{-4}$ ), results in emissions of 0.06 mg/GWh, an amount which is negligible within the context of life cycle analysis.

## 5. ACKNOWLEDGMENT

This work was supported by the Solar Technologies Program, Conservation and Renewable Energy, under Contract DE-AC02-76CH000016 with the US Department of Energy.

## 6. REFERENCES

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